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M. Desmaison-Brut, D. Tetard, C. Tixier, Catherine Faure, E. Chabas. Mechanical Properties and Oxidation Behaviour of Electroconductive Ceramic Composites. 10th International Conference of the European Ceramic Society, Jun 2007, Berlin, Germany. pp.1315-1320. hal-00282732

HAL Id: hal-00282732

<https://hal.science/hal-00282732>

Submitted on 28 May 2008

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Mechanical Properties and Oxidation Behaviour of Electroconductive Ceramic Composites

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Abstract

Dense electroconductive ceramic-ceramic composites silicon carbide-hafnium diboride (SiC-HfB₂) and silicon carbide-hafnium carbide (SiC-HfC) were obtained by Hot Pressing (HP). In view of the results, the high performance composite grade SiC-HfB₂ has also been elaborated by Hot Isostatic Pressing (HIP). For 25 mol % HfC or HfB₂ content, the resistivity was low enough to allow electrodischarged machining (EDM).

The mechanical and thermal properties as well as the wear and oxidation behaviours were evaluated and compared.

The electroconductive boride composite (75-25 mol% SiC-HfB₂) exhibits high mechanical properties. The benefit of the diboride phase's presence is also noticed in fluent oxygen, up to 1450°C. The SiC-HfB₂ composite is as resistant as silicon carbide. This behaviour may be related to the formation of a borosilicate based oxide layer containing hafnium phases, which plays the role of a coating and which limits the B₂O₃ evaporation.

Keywords: ceramic composites, silicon carbide, hafnium carbide, hafnium diboride, mechanical properties, wear, oxidation resistance, electrodischarged machining.

Introduction

Silicon carbide, a highly covalent bonded ceramic, is difficult to densify without small amounts of additives. A variety of sintering aids were tested during the last decades including yttria, alumina, boron, boron nitride, carbon, silicon nitride... The studies have provided evidence that the liquid phase sintering of SiC proceeds via a classical solution-reprecipitation mechanism [1-5]. Nevertheless, expensive cost for machining parts limits uses of this attractive engineering material. An alternative technique to diamond machining is to use electrodischarged machining (EDM).

An approach to ECCs (electroconductive ceramics) is to combine insulating ceramics as Si₃N₄ and SiC with an electrically conductive phase, e.g. TiC, TiB₂, ZrB₂ yielding reinforced ceramic-ceramic composites.

Materials consisting of silicon carbide and metallic diboride (TiB₂, ZrB₂, HfB₂) offer a good combination of properties and a high temperature resistance that make them candidates for air frame engines, heat exchanger tubes for industrial furnaces, aerospace parts... The studies are mainly concerned with the SiC-TiC and SiC-TiB₂ composites [6-13], the addition of the titanium

diboride to the main silicon carbide phase, offers potentiality for uses at temperature greater than 1000°C. In this work, electroconductive composites were produced by the addition of a secondary HfC or HfB₂ phase to SiC.

Experimental

The materials investigated are listed in Table 1.

The starting powders were mixed and dispersed with ultrasonic assistance in petroleum ether for few seconds. The mixture was then dried at 60°C and sieved at 32 µm.

grade	SiC Stark UF10	HfC Cerac	HfB ₂ A. Aesar
Average grain size (µm)	0.80	1.41	9.51
Impurities wt%	O: 0.02 Fe: 0.01 Al: 0.01	Zr: 0.29	Zr < 2

Table 1. Some characteristics of the powders

All the grades (50-50 and 75-25mol%) were hot pressed at 1830°C, 40 MPa for 3 hours.

The 75-25 mol% SiC-HfB₂ mixture was cold isostatically pressed at 200 MPa and the crude cylinder was hot isostatically pressed within a silica container at 1850°C, 185 MPa and a 90 minutes dwell time.

Silicon (0.5 wt%) or silicon plus YAG (Y₃Al₅O₁₂) additives (2 wt%) were added to the main phase(s) to reach total densification.

The room temperature strength measurements were done on 4x4x25 mm³ polished and edged bars with a 3-points bending technique (WOLPERT apparatus). The Knoop microhardness was carried out by using a SHIMADZU apparatus (applied load 300 g for 10 seconds). The fracture toughness was measured by the Single Edge Notch Beam method on bars of the same size with a triangular carving of 1 mm depth. Elastic properties have been obtained with a Grindo Sonic apparatus at room temperature on 40 mm diameter and 4 mm thick discs. The wear resistance was investigated on a Phenix tribometer (Plint TE-66), in air and in presence of a SiC solution (0.21g/mL) with a steel bearing ball (AISI 52100 steel) of 25 mm diameter rotating at 120 revs/min under a 1N load. Tests were performed at five different rotations (300 to 1100) on polished specimen (Ra = 0.01 µm). Phases and

microstructural analyses of samples surfaces and cross-sections were carried out by X-Ray diffraction (XRD, SIEMENS D5000), SEM and EDS microanalysis (PHILIPS XL30).

Isothermal oxidation tests were performed on cubic samples ($4 \times 4 \times 4 \text{ mm}^3$) with a SETARAM microbalance at temperatures up to 1450°C in flowing oxygen (10 L/h). Non-isothermal tests were done in the same conditions with a $2^\circ\text{C}/\text{min}$ heating rate.

Results and Discussion

Elaboration

All the final relative densities (dr%) reaches 99% at the exception of HfC (Table 2). The complete sinterability of the monolithic HfC or HfB₂ ceramics and of the 50-50 mol% composites are achieved with 0.5% of silicon, but the monolithic SiC and the 75-25 mol% SiC-HfB₂ or SiC-HfC materials need an additional 2% YAG. The formation of a liquid phase noticed at 1350°C and located at grain boundaries is presumably HfSi₂, this liquid phase stimulates the sintering (Fig. 1).

Produit	HfC (Cerac)	HfB ₂ (A. Aesar)	HfC/SiC 25/75 mol%	HfB ₂ /SiC 25/75 mol%	SiC Starck
Density (%)	98,7	99,3	99,0	99,9	99,9
Hardness (GPa)	21±0,1	24±0,5	25,5 ±0,2	25,5±0,2	25,8 ±0,2
Young modulus E (GPa)	451	559	447	469	437
Shear modulus G (GPa)	188	243	190	202	187
Flexural strength σ_F (MPa)	490 ±10	568 ±12	515 ±10	546 ±11	926 ±18
Toughness K _{IC} (MPa $\sqrt{\text{m}}$)	6±0,4	7,5±0,1	5,7±0,4	7±0,1	5,9±0,2
Therm. Cond λ (W/m.K)	20±1	126±6	80±4	114±5	108±5
α ($10^{-6}/\text{K}$)	5,5	5,3	4,7	6,5	4,7

Table 2. Thermomechanical properties of the grades

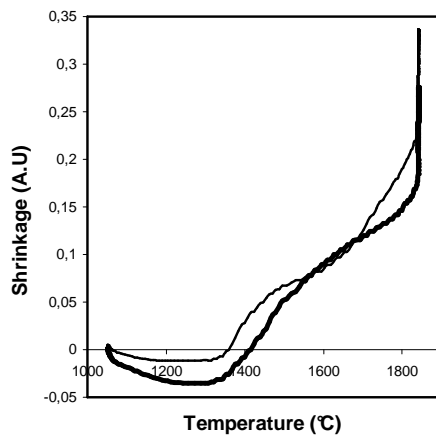


Fig.1. Density curves, $15^\circ\text{C}/\text{min}$, dwell at 1830°C

Concerning the composites, a good dispersion of the secondary phase is noticed (Fig. 2). No reaction is observed between the two main phases. The alpha SiC (6H) phase is detected by XRD as it is the most stable form of SiC at high temperature. Elongated-shaped grains of the SiC phase are not observed on SEM which show essentially equiaxed grains ranging in size from 1 to $4 \mu\text{m}$. There is no evidence of grain growth for SiC and the composite grades. The boride or carbide particles are supposed to control the SiC matrix grain size by a pinning mechanism. On the contrary, monolithic HfC and HfB₂ ceramics present a non negligible increase of the grain size.

Thermomechanical properties

Microhardness, flexural strength and toughness have been performed at room temperature (Table 2). We will mainly focus on SiC and on the HP 75-25 mol% grades of highest properties. Unfortunately, the hiped SiC-HfB₂ material does not show real improvement of the mechanical properties. Nevertheless, the densification has occurred earlier by hiping (half dwell time).

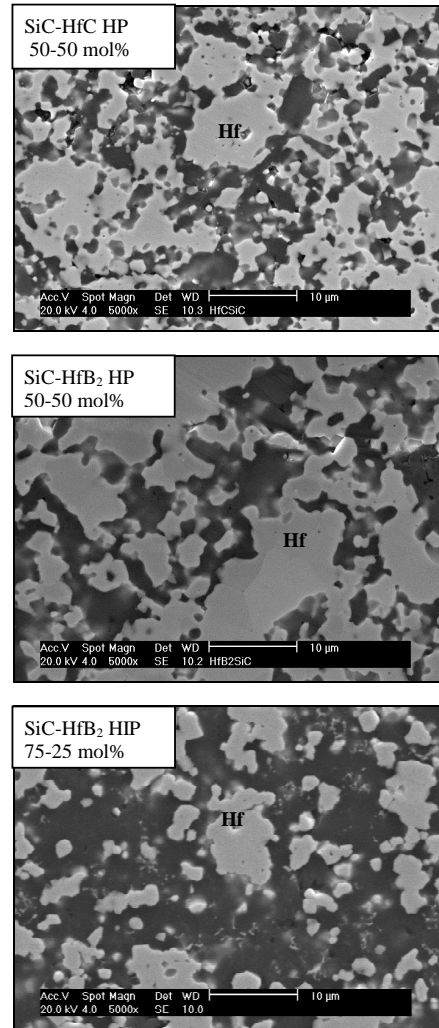


Fig.2. Polished surfaces of the composites

There is no damaging effect of an additional 25 mol% HfC or HfB₂ to the SiC ceramic as the Knoop microhardness values of the three grades reach 25 GPa. By comparison, a value of 20.5 ± 1.6 GPa was obtained on a 20-80 vol% SiC-HfB₂ composite [13].

Concerning the RT flexural strength, the monolithic silicon carbide is clearly more resistant. This behaviour can be explained by the nature of the complex silicon plus YAG intergranular phase as, presumably, reaction occur between the silica surrounding the SiC or/and the silicon grains and the YAG phase. The high value obtained is the result of a strong interface but the fracture mode is still mainly intergranular (Fig. 3). The relatively small grain size of the SiC and composite materials may also favour this type of rupture.

A relatively low difference exists between the SiC and the HfB₂ thermal expansion coefficients (CTE) of the two phases. Classically, for composites, a weaker or a strong interface ensures from the difference between the thermal expansion coefficients of the main phases, but the presence of the liquid phase at grain boundary has to be taken into account.

Concerning the pure hafnium carbide or diboride, very small residual pores are observed in some HfC grains of the monolithic carbide and transgranular rupture of biggest grains is more often noticed.

It has been shown that the strength increases but the toughness decreases with increasing alpha SiC content [14-16].

Contrary to literature data, the significant improvement of the SiC-HfB₂ toughness may not be related to the presence of elongated grains [14]. The high values are mainly due to crack deflexion with some possible contribution from microcracking.

The thermal conductivities of the monolithic and composite materials are shown Table 2.

As already published, the conductivity of HfB₂ is six times higher than the HfC one [16]. In comparison with SiC, the SiC-HfB₂ composite exhibits a higher thermal conductivity.

The higher elastic constants of HfB₂ than SiC induce highest RT values of the SiC-HfB₂ Young and Shear moduli [17,18].

The wear coefficients of the two borides are very similar (6.2 and $6.7 \cdot 10^{-8} \text{ mm}^2.\text{N}^{-1}$) not so far from the value of tungsten carbide WC/Co ($0.1 \cdot 10^{-8} \text{ mm}^2.\text{N}^{-1}$), material often used for cutting tools.

The SiC-HfB₂ composite has a lower wear rate than the monolithic SiC material, as would be expected from its superior fracture toughness (Fig. 4) [19-23]

The pure HfC material shows the highest value. The grains removal may be correlated to the brittleness of the boundary phase and to the small porosity.

The addition of 25% of hafnium diboride or hafnium carbide in the silicon carbide matrix is high enough to perform EDM as shown on Fig. 5 (copper electrode, 1 A power) [24].

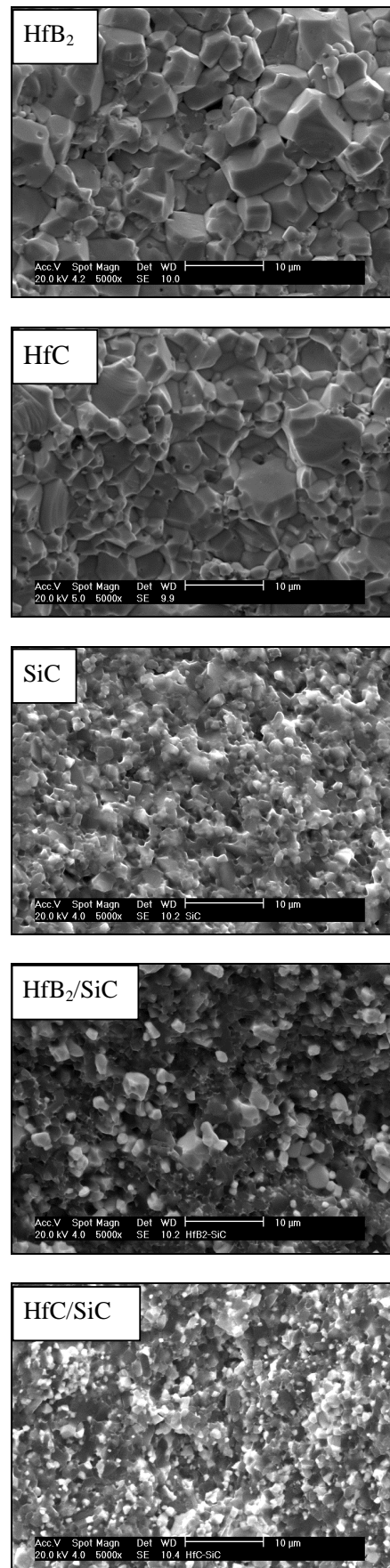


Fig.3. Fracture surfaces of the different grades

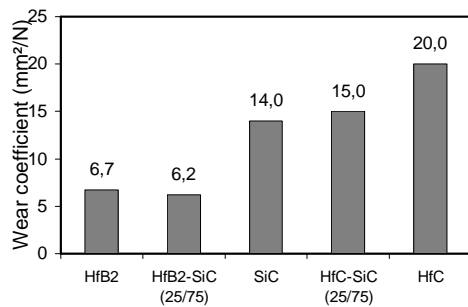


Fig.4. Wear coefficient of the different HP grades



Fig.5. Disk obtained by EDM (SiC-HfB₂, 75-25 mol%) diameter 25 mm, thickness 2,5 mm

Oxidation

SiC based composites containing diborides of the transition metals (Hf or Zr) are known as ultra-high temperature ceramics (UHTCs) [25-30].

The monolithic and composites grades are corroded in pure and fluent oxygen and their oxidation behaviours are compared. The HfC and SiC-HfC ceramics start to oxidize at 800°C as seen on the non-isothermal curves (Fig. 6). The dwell observed on the composite curve arises after the complete consumption of the HfC phase that leads to a hafnium powder. Then occurs the oxidation of the HfC depleted SiC phase.

On the opposite the HfB₂ and SiC-HfB₂ materials are more oxidation resistant, this last grade is as performant as the SiC material up to 1450°C.

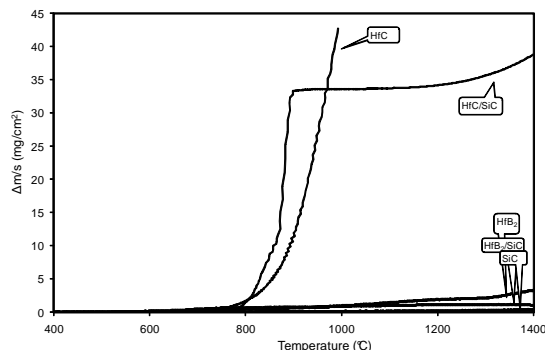
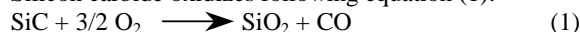
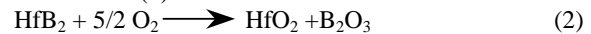


Fig.6. Non-isothermal oxidation curves (2°C/min)

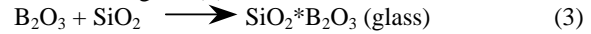
Silicon carbide oxidizes following equation (1):



The preferential oxidation of HfB₂ occurs according to the reaction (2):



Above 1000°C, the vaporisation of B₂O₃ should become important but as the main SiC phase slightly oxidizes, SiO₂ could react with B₂O₃ to form a borosilicate glass (3):



This glassy phase has a higher melting point, higher viscosity and a lower vapour pressure than B₂O₃ and the oxygen transport through the oxide scale depends on these parameters.

At 1450°C, the isothermal kinetic of the SiC-HfB₂ composite cube follows an initial parabolic stage before linearisation. The specimen is covered with a silicon-boron-aluminum oxide glassy phase. Al, Y and Hf are detected near the surface by EDS analysis (Annex 1). Mixed oxides (few amount of HfSiO₄, Y₂Si₂O₇ and the aluminoborate Al₁₈B₄O₃₃) are formed. Below the oxide layer, a SiC depleted sublayer exists in accordance with the literature data on the SiC-ZrB₂ composite [28].

A porosity line is noticed at the oxide-core interface.

The thickness of the oxide scale increases with temperature and time limiting the inward oxygen diffusion and the outward transport of gaseous CO and B₂O₃ species.

Conclusion

Dense ceramic materials are densified either with silicon (0.5%) or silicon and YAG (2.0%) by hot pressing or hot isostatic pressing.

The addition of 25 mol% of metallic boride or carbide in the silicon carbide matrix allows EDM.

The performances of the HfC based materials are the lowest. The 75-25 mol% SiC-HfB₂ ceramic composite is produced without detrimental effects on the main SiC matrix properties with the exception of the SiC strength (high value of more than 900 MPa).

Besides, this boride composite grade (75-25mol% SiC-HfB₂) is very resistant to oxygen oxidation up to 1450°C. A viscous borosilicate glass embeds the core and limits the inward oxygen diffusion and the outward boron sesquioxide release through the oxide scale.

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Annex 1: SEM and EDS of samples oxidized at 1450°C during 24h
a-f: SiC-HfB₂ (75-25) cross-sections; g,h: SiC-HfB₂ (75-25) surfaces; i,j: SiC surfaces

